

BUSINESS CONFIDENTIAL

TO: R. F. Kayser
FROM: D. L. Bailey
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TECHNOLOGY MANAGER'S
REPORT
BUSINESS DEPARTMENT 33
BUSINESS AREA 57

SILICONES OPERATIONS
HIGHLIGHTS

Construction of suitable analytical equipment for monitoring the type of epitaxial silicon to be obtained from dischlorosilane and trichlorosilane is well underway. The 220 volt - 3 phase service and 5 kw induction heating unit have been installed, permitting testing of materials, such as graphite slabs and silicon wafers. Resistivity measurements made with our equipment on wafers supplied by Motorola agree quite well with figures reported by them.

The possible effects of cross-contamination during distillation of A-186, A-187 or A-1100 coupling agents in the Plant High Vacuum Distillation System were examined. Although A-1100 reacts readily with A-186 and A-187, both at ambient and elevated temperatures, the reaction is not catalytic. Rather, a one-to-one adduct appears to be formed, followed by transesterification. No gells or high viscosity products were obtained under a variety of conditions. Therefore, only ordinary cleanup precautions need to be taken in the distillation of these coupling agents.

Silicone fluids containing silanic hydrogen can be equilibrated rapidly at higher temperatures (up to 60°C) with Amberlyst 15 catalyst without significantly increasing their level of contamination with sulfur dioxide. The reactivity of these fluids is comparable in silylation reactions to those prepared by sulfuric acid equilibration.

A study of the effects of molecular weight and functionality has shown that these are significant factors in the properties of Y-7086 (Y-4828 quaternary organosilicone in ethanol) for LaMaur, Inc. The laboratory program also was successful in resolving several process variables encountered in making this product. Quite surprisingly, the presence of dimethylamine hydrochloride in the product has a profound effect on viscosity-build of the aqueous solution.

Since the diol content in polyethers is a critical factor in preparing polyether intermediates for surfactants a reliable test method for determining the amount of diol present is being developed. Aqueous solution viscosities of the resultant surfactants appear to be closely related to the diol contents

RESEARCH AND DEVELOPMENT DEPARTMENT
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SISTERSVILLE, WEST VIRGINIA

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Silicones Operations
Highlights - Continued

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of the starting polyethers. This measurement is sensitive with polyethers containing one to five weight percent diol.

The MQ resin surfactant, Y-6364, of interest in frothed vinyl foam was prepared in the Pilot Plant 50-gallon kettle for the first time starting with silicon tetrachloride. The partial ethoxy ester of silicon tetrachloride was cohydrolyzed with trimethylchlorosilane; then condensed with potassium hydroxide. The material meets target properties and is equivalent to the Froth Density standard. The use of partial ester in place of tetraethyl orthosilicate shows a considerable saving on raw material costs.

The first Pilot Plant preparation of Y-6426, a polyether modified MQ resin surfactant, ran smoothly. The process involved the platinum catalyzed addition of methylchlorosilane to benzyl capped APEG-350 (Y-6310), followed by cohydrolysis with trimethylchlorosilane and tetraethyl orthosilicate. The preparation appears to meet target properties. A sample has been sent to Tarrytown for flammability test.

The product quality as indicated by the production reject rate was 2.0% for July, a remarkable low record number.

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A. Trichlorosilane and Related Compounds.

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Construction of suitable analytical equipment for monitoring the type of epitaxial silicon to be obtained from dichlorosilane and trichlorosilane is well underway. The 220 volt - 3 phase service and 5 kw induction heating unit have finally been installed, permitting testing of materials, such as graphite slabs and silicon wafers. Resistivity measurements made with our equipment on wafers supplied by Motorola agree quite well with figures reported by them.

A total of 2,308 pounds of dichlorosilane was produced this month. After sequestering the product with iodine, the vapor drawn from the product cylinders showed 0.1 parts per billion Phosphorous and 0.05 to 0.18 parts per billion Boron. The average production rate of 5.6 lb/hr was below the estimated 6.9 lb/hr due to several time inefficiencies which can be improved. Actual process time was 54% of the total campaign time due mainly to replacement of gaskets and diaphragm valves. It is being determined whether the dichlorosilane or trimethoxysilane process is the culprit causing these failures since both are produced in the same unit.

B. Coupling Agents.

The possible effects of cross-contamination during distillation of A-186, A-187 or A-1100 coupling agents in the Plant High Vacuum Distillation System were examined. Although A-1100 reacts readily with A-186 and A-187, both at ambient and elevated temperatures, the reaction is not catalytic. Rather, a one-to-one adduct appears to be formed, followed by transesterification. No gells or high viscosity products were obtained under a variety of conditions. Therefore, only ordinary clean-up precautions need be taken in the distillation of these coupling agents.

Improved analytical methods recently developed by the Analytical Group for us indicate that A-174 (methacryloxypropyltrimethoxysilane) contains a much higher level of hydroquinone (~1200 ppm) than previously believed (300-500 ppm). The new procedure consists in silylation of hydroquinone with 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane and the use of a flame ionization detector. DPPD (N,N'-diphenyl-p-phenylene-diamine) concentration was found to be less than 10 ppm for the Kloss column distilled A-174 and ca. 150 ppm for the molecular still distilled material. Results obtained from VPC and colorimetric methods for the DPPD determination appears to be in good agreement.

Arochlor 1248, a chlorinated biphenyl, used as a pot chaser in the distillation of B-cyanoethyltriethoxysilane (CNE) and A-1100, is being discontinued by the manufacturer because of toxicity and environmental problems. Three polyethers were studied as possible replacements: Ucon 50HB260, 50HA1100 and Y-6044. Within the limits of VPC analysis, all are equivalent and any one should be suitable as a replacement for Arochlor 1248. Moreover, they are compatible with CNE, A-1100 and Arochlor 1248. After 200°C at 24 hours, followed by product stripping, the resulting heavies are low in viscosity (~100 cs. for 50HB260) and easily handled. Samples of heavies are being supplied for compatibility testing in the waste disposal system.

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C. Silicone Resins.

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Samples from a recent Pilot Plant (K-21-1) preparation of R-860 show very little methyl loss occurring during the hydrolysis, esterification and two hour reflux steps. The bulk of the methyl loss is taking place in the final product strip. Enough specification R-860 was prepared in the last campaign to fulfill our current needs, however, it is evident that the reproducibility of the R-860 methoxy content is poor. Initial laboratory work indicates the side reaction of methanol and HCl to give methyl chloride and water is much more critical than originally believed. Means of controlling this unwanted side reaction are being sought.

D. Silicone Oils.

Physical tests and microscopic examinations indicate American Chemet copper catalysts have little or no organic coating and adhere tenaciously to silicon particles. This is considered of significance in the direct reaction of methyl chloride with silicon and may account for the good results obtained with these catalysts. A chemical microscopic apparatus will be used to compare the activity of ACC copper and Robertson copper with silicon and methyl chloride with the objective of establishing the temperature at which copper and silicon appear to be affected.

Amberlyst resins continue to be of interest as equilibration catalysts for dimethylsilicone oil systems, in particular, fluids containing SiH substituents. Silicone fluids containing silanic hydrogen can be equilibrated rapidly at higher temperatures (up to 60°C) with Amberlyst 15 catalyst without significantly increasing their level of contamination with sulfur dioxide. The reactivity of these fluids is comparable in silylation reactions to those prepared by sulfuric acid equilibration.

Further insight has been obtained on the side reactions which occur during the base catalyzed depolymerization of dimethylsilicones. For example, at elevated temperatures (>200°C), and in the presence of promoters, such as trioctylphosphine oxide, disproportionation of dimethylsiloxane units to trimethylsiloxane and methylsiloxane units, and methyl cleavage reactions with protolytic reactants, such as water, alcohols and amines, are significantly increased. Rates and ceiling temperatures for these reactions are being determined.

The feasibility of making Y-4177 (a 37% solids emulsion of L-45 oil, 350 cstc) in the Manton-Gaulin Homogenizer was investigated. Homogenization pressure, process rate, and number of passes (total 24 combinations) were varied to determine optimum process conditions. Stability problems were encountered in every batch. The premix was formulated as 37%; better homogenization should be obtained by using a high-solids premix with dilution to 37% solids.

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D. Silicone Oils - Continued.

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LaMaur, Inc. has a requirement for a silicone, Y-7086 (Y-4828 quaternary organosilicone in ethanol), to be used in their Temptra Tone product. They evidently require a Y-7086 that has partial water solubility and which shows a viscosity build as an aqueous solution. A limited laboratory program has been initiated here to provide a suitable material. Several samples were made by varying the starting silicone molecular weight and functionality. The process consists of the preparation of the silicone SiH fluid, reaction with allylglycidyl ether, followed by amination with dimethyl amine and quaternization with methyl chloride in ethanol solution. The first two steps were straightforward and reproducible. Several problems were encountered during the amination step resulting in high viscosities and gells. This was resolved by keeping an excess amine at all times to complete the desired reaction. The process is reproducible. Quaternization is completed after the amine step as soon as possible and no problems were encountered. Evaluation of the sample prepared shows that molecular weight and functionality are factors. It was also found that by adding dimethylamine hydrochloride to double the original chloride content, a dramatic effect on the viscosity-build is observed (6 to 50 cps).

The first 500-gallon batch of crude hexamethyldisilazane was prepared without difficulty. Crude properties were the same as the 50-gallon batches. Purification of the crude required a double distillation to reach 98% purity. The cost for reaching 85-90% purity has been calculated and is significantly less. The lower purity is of interest to a second customer.

E. Surfactants.

The diol content in polyethers is critical for the allylation process (allyl chloride capping) in preparing polyether intermediates for surfactants (e.g., formation of diallyl polyether causes crosslinking with polyfunctional $\equiv\text{SiH}$ fluids to give high viscosity or gellation). With our renewed interest in the allylation process, it is imperative that a reliable test method be developed. By making use of an earlier finding (by others) that the aqueous viscosity of the resultant surfactant is most sensitive to the diallyl content, we have now demonstrated the feasibility of using this technique to differentiate "high" from "low" diols. For example, a silicone-polyether copolymer from Y-4569 polyether and Y-4860 $\equiv\text{SiH}$ fluid gave an aqueous solution (40%) viscosity of 4000 cps while the diallyl (5 wt.%) spiked Y-4569 gave a copolymer of aqueous solution viscosity 184,000 cps. A systematic study of various polyethers with various diol levels is underway.

A recent production batch of L-77 organosilicone with a high cloud point (40°C) has prompted a study into the factors that affect cloud point. Surprisingly, addition of 1, 2, 5 and 10 weight percent 3-ethyl heptamethyl trisiloxane to L-77 increased the cloud point from 12°C to 15, 48, 44 and 40°C respectively. Addition of 2, 5 and 10 weight percent A-1701 [MD'M equilibrium adduct of Y-6044 (MeO capped APEG-350)] increased the cloud point

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E. Surfactants (Continued).

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of L-77 (12°C cloud point) to 13, 15 and 50°C respectively. The effect of acetal and diallyl on L-77 cloud point is also being evaluated.

The MQ resin surfactant, Y-6364, of interest in frothed vinyl foam was prepared in the Pilot Plant 50-gallon kettle for the first time starting with silicon tetrachloride. The partial ethoxy ester of silicon tetrachloride was cohydrolyzed with trimethylchlorosilane; then condensed with potassium hydroxide. The material meets target properties and is equivalent to the Froth Density standard. The use of partial ester in place of tetraethyl orthosilicate shows a considerable saving on raw material costs.

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L-5410 rigid urethane surfactant which has been rejected for failing the premix compatibility test was recovered in the Pilot Plant using the laboratory method of dilute acid treatment followed by neutralization and dehydration. Two 40-gallon batches were run with both yielding specification grade L-5410. Scaleup to the 4000-gallon kettle in Polymers II was not successful, apparently due to the longer process time normally encountered in the larger equipment.

A 90HA550 polyether and its methyl carbamate capped derivative (Y-6412) were successfully prepared in the Pilot Plant. Hydroxyl analysis by IR indicates 94% capping. The capping process is lengthy due to the precautions involved in handling methyl isocyanate. The only problem occurred while stripping excess methyl isocyanate. Strong fumes from the scrubber water sump cleared the area of personnel. Y-6412 samples have been sent to Tarrytown for tin analysis and general evaluation.

F. Quality Control.

The product quality as indicated by the production reject rate was 2.0% for July, a remarkable low record number.

A new raw material specification manual has been distributed. This now contains the inter-company purchases of materials used for silicones. The materials purchased outside the corporation are now under review for inclusion in the manual.

The silicones producers, through the Industrial Hygiene Foundation, are attempting to start a program for environmental pollution control. The meeting was attended in Pittsburgh, and our toxicological data files have been reviewed to determine what information might be sent to them. Summary information from Mellon

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F. Quality Control (Continued).

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reports have been sent to our Medical and Toxicology Department for Dr. K. S. Lane to prepare appropriate analytical statements.

In the semi-conductor area, the trichlorosilane quality has been good. Production is now achieving low carbon concentrations, some lots having less than 1 ppm. The use of HCl in the reactor having high carbon bearing impurities was a major cause of this quality problem in March and April.

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